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Depth Profiles of Persistent Organic Pollutants in the North and Tropical Atlantic Ocean

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1 **Depth profiles of persistent organic pollutants**

2 **in the North and Tropical Atlantic Ocean**

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9 **ABSTRACT**

10 Little is known of the distribution of persistent organic pollutants (POPs) in the deep ocean.
11 Polyethylene passive samplers were used to detect the vertical distribution of truly
12 dissolved POPs at two sites in the Atlantic Ocean. Samplers were deployed at five depths
13 covering 26-2535 m in the northern Atlantic and Tropical Atlantic, in approximately one
14 year deployments. Samplers of different thickness were used to determine the state of
15 equilibrium POPs reached in the passive samplers. Concentrations of POPs detected in the
16 North Atlantic near the surface (e.g. sum of 14 polychlorinated biphenyls, PCBs: 0.84 pg
17 L⁻¹) were similar to previous measurements. At both sites, PCB concentrations showed
18 sub-surface maxima (tropical Atlantic Ocean – 800 m, North Atlantic – 500 m). Currents
19 seemed more important in moving POPs to deeper water masses than the biological pump.
20 The ratio of PCB concentrations in near surface waters (excluding PCB-28) between the
21 two sites was inversely correlated with congeners' sub-cooled liquid vapor pressure, in
22 support of the latitudinal fractionation. The results presented here implied a significant
23 amount of HCB is stored in the Atlantic Ocean (4.8-26 % of the global HCB environmental
24 burdens), contrasting traditional beliefs that POPs do not reach the deep ocean.

25

26 INTRODUCTION

27 Open ocean seawater measurements of persistent organic pollutants (POPs) are scarce
28 due to the difficulties associated with the sampling procedure, contamination and costs of
29 cruises.¹ There are even less data on POPs in the deep ocean, since most of the
30 measurements of POPs in the open ocean were limited to surface seawater. Little is known
31 of the role played by deep ocean compartments in storing POPs from the surface.² Of the
32 few previous measurements of deep oceanic POPs, two were based on active sampling,
33 targeting polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs)
34 in deep waters in the North Atlantic (near the South-Western edge of the Porcupine Abyssal
35 Plain and around Iceland)³, and PCBs in the central Arctic Basins (Nansen, Amundsen,
36 and Makarov).⁴ More recently, concentrations of PCBs, PAHs, hexachlorobenzene (HCB)
37 and dichlorodiphenyldichloroethylene (DDE) were detected using passive sampling at 0.1-
38 5 km depth in the Irminger Sea, the Canary Basin and the Mozambique Channel.² These
39 studies reported the existence of POPs in the deeper ocean and indicated that the deep
40 oceans could be an important compartment for storing POPs.

41 The study by Booij et al.² was the first to use passive sampling (semipermeable
42 membrane devices, SPMDs) to study the POPs vertical distribution in the ocean. Even
43 though active sampling has been traditionally used, it bears the disadvantage of extensive
44 labor and extreme care of controlling blank levels.² Polyethylene sheets (PEs) is one
45 common form of passive sampling devices. It has many advantages including simplicity in
46 its chemical makeup, low cost, easy handling and a high enrichment of POPs.⁵ Passive
47 sampling was recently suggested a useful tool used monitoring POPs in open ocean.⁶

48 Unlike active sampling, passive samplers only take up ‘truly’ dissolved compounds, not
49 those bound to colloids.

50 Under the circumstances that the time to reach equilibrium is not known, the sampling
51 rate (R_s) can be used to derive the state of equilibrium upon retrieval. One way to calibrate
52 R_s is to use performance reference compounds (PRCs). PRCs are chemicals that are
53 artificially made which share similar properties to target compounds. However, due to the
54 extensive long time of pre-spiking samplers with PRCs, another approach has been
55 suggested by Bartkow et al.⁷ using different thickness to confirm that equilibrium has been
56 reached.

57 In this study, polyethylene passive samplers of different thickness were deployed at two
58 deep ocean sites (eastern Fram Strait and Cape Verde Abyssal Plain) in the Atlantic Ocean
59 to determine vertical distributions of truly dissolved concentrations of several classes of
60 POPs, including PCBs, organochlorine pesticides (OCPs), polybrominated diphenyl ethers
61 (PBDEs) and PAHs. The objectives of this study were to (i) measure a wide range of POPs
62 in vertical profiles at two locations in the North Atlantic; (ii) contrast north-south and
63 surface-to-deep gradients and (iii) improve the knowledge of fate and transport of POPs to
64 the deep ocean.

65

66

67 **METHODS**

68 **Sampling**

69 *PE sheet samplers preparation*

70 PEs of three thickness were used in the study: 800, 1600 and 50 μ m. Polyethylene
71 samplers preparation details are given in Supporting Information. Only 50 μ m PEs were
72 pre-spiked with PRCs using the method described by Booij et al.⁸

73

74 *Deep mooring sampling*

75 Samplers were strung on stainless steel wires and attached to stainless porous cages.
76 Cages were attached to deep mooring systems and deployed in North Atlantic (79° N, 4°
77 E) and Tropical Atlantic (25° N, 38° W) (Figure 1). Deployment depths were 213 m, 468
78 m, 1173 m, 1736 m and 2535 m for the North Atlantic and 26 m, 84 m, 251 m, 800 m and
79 1800 m for the tropical Atlantic Ocean, respectively. Two sampling sheets were deployed
80 at each depth. Sampling time was around one year for both deployments (North Atlantic:
81 July 21st 2012 ~ July 8th 2013; Tropical Atlantic: Sep 14th 2012 ~ Oct 1st 2013). Current
82 velocities were also measured at different depths by current meters during the entire
83 mooring period. Current velocities were averaged over the deployment time for discussion
84 in this paper. After samples were collected, they were wrapped in clean aluminum foil,
85 shipped back to lab and stored at -4°C until analysis.

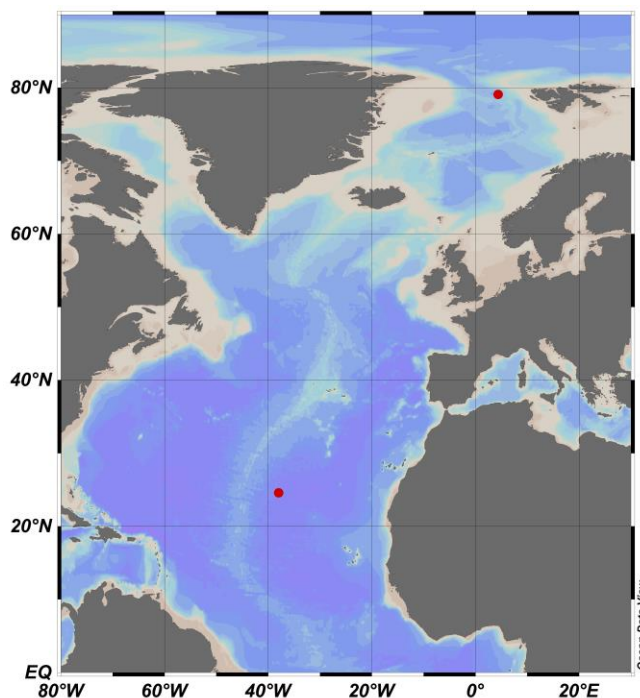


Figure 1. Sampling locations of the deep moorings in 2011-12.

Sample analysis

Sample extraction

After being wiped clean using Kimwipes, PEs were cut into pieces and extracted in hexane overnight twice with surrogate injected. Extracts were then concentrated into GC-vials and analyzed by GC-MS/ GC-MS-MS. Details on sample extraction and instrumental analysis are given in the Supporting Information.

Quality assurance/quality control

Matrix spike and lab blanks were performed for each batch of approximately 10 samples. Field blanks were taken during the North Atlantic deployment. All blanks were extracted in the same method as samples. Limits of detection (LOD) were derived from field blanks

and determined by three times the standard deviation of field blank samples. Detailed QA/QC information are in the Supporting Information (detection limits of all the compounds quantified in this study are given in Table S3; recoveries are given in Table S4).

PE concentration (C_{PE}) conversion to environmental concentration

Concentration of target compounds in the PEs (C_{PE} , ng g⁻¹) were converted to freely dissolved water concentrations (C_w , kg L⁻¹) by equation (1)

$$C_w = \frac{C_{PE}}{K_{PEw}} \times \frac{1}{\% \text{ equilibrium}} \quad (1)$$

where

K_{PEw} is the compound specific partitioning coefficient between PE and water (L kg⁻¹) whose temperature correction for K_{PEw} was done using equation (2), and %equilibrium is the percentage of equilibrium achieved by individual compound in the sampling period which is given by equation (3)

$$K_{PEw}(T) = K_{PEw}(298) e^{\frac{(\Delta H_{PEw}/R)}{\{ \frac{1}{298} - \frac{1}{T} \}}} \quad (2)$$

where

$K_{PEw}(T)$ and $K_{PEw}(298)$ are PEw partitioning coefficients at temperature T (K) and 298 K, respectively;

ΔH_{PEw} is the enthalpy of PEw partitioning (kJ mol⁻¹);

and R is the universal gas constant (8.3143 J mol⁻¹ K⁻¹);

$$\% \text{ equilibrium} = 1 - e^{\left(\frac{-R_s t}{K_{PEw} V_{PE}} \right)} \quad (3)$$

121 where

122 R_s is the sampling rate (L/day) for one whole sampling sheet;

123 t is sampling time (days); and

124 V_{PE} is the volume of the PE (L).

125

126 **Estimations of sampling rates**

127 *Using different thickness*

128 Sampling rates were estimated based on the assumption that PEs deployed at the same
 129 depth/cage were exposed to the same truly dissolved concentration (C_w), and that the same
 130 sampling rate applied to all compounds. R_s pairs were assumed to be from different
 131 combinations of integers from 1~X L/day (X=100, 50, 40, 30 20, 10). For each
 132 combination, %equilibrium was calculated using equation (6) and the environmental
 133 concentration was further determined using equation (1). The aim was to find the exact pair
 134 of R_s that minimizes the total of standard deviations of all detected compounds. The total
 135 of standard deviations is defined as

$$136 \quad \sum_{i=1}^n s_i \quad (4)$$

137 where

138 n is the number of pairs of data, and

139 s is the standard deviation of the derived environmental concentration (x_j) by the two PEs
 140 in the same cage

$$141 \quad s = \sqrt{\frac{1}{N-1} \sum_{j=1}^N (x_j - \bar{x})^2} \quad (N=2) \quad (5)$$

142

143 *Using PRCs*

144 Site specific sampling rates were also calculated via a nonlinear least-squares method
 145 adapted from Booij and Smedes.⁹ This method only applies to PEs that were pre-spiked
 146 with PRCs, i.e., the 50 µm thick ones in the tropical Atlantic 84 m and 251 m deployment.

147

148 **Latitudinal Fractionation**

149 The ratio of the concentration of each individual compound near the surface layer (231
 150 m) at 79° N divided by the surface concentration at 24° N (26 m) was plotted as a function
 151 of their subcooled liquid vapor pressure (P_L).

152

153 **Estimation of water age using chlorofluorocarbons, CFCs**

154 Transient tracers, including CFCs, are useful as a water mass tracer because their
 155 atmospheric concentration can be uniquely related to a calendar year. In turn, water at the
 156 ocean surface records this unique concentration based upon air-water gas partitioning. The
 157 equilibrium partitioning between CFC concentration in the air and water is described by
 158 Henry's Law. Dissolved CFCs concentration C_w (mol kg⁻¹) at the locations of interest were
 159 obtained from Carbon Hydrographic Data Office (CCHDO). Temperature and salinity data
 160 were obtained from the same origin and were used for deriving the Henry's Law Constant
 161 H (mol kg⁻¹). The molar ratio of CFCs in the atmosphere χ (mol CFC mol⁻¹ air) were then
 162 calculated using

$$163 \quad \chi = \frac{C_w}{H} \quad (6)$$

164 The results represented the molar ratio of CFCs in the atmosphere when the water were
165 at the surface. They were compared to recorded atmospheric CFCs concentrations from
166 Carbon Dioxide Information Analysis Center (CDIAC) to determine the calendar year
167 when the water was last contact with the air.¹⁰ SF₆ data were of the highest priority if
168 available; if not, CFC-12 data were used instead.

169

170 **RESULTS AND DISCUSSION**

171 **Truly dissolved surface concentrations of POPs**

172 *Tropical Atlantic*

173 \sum_{14} PCBs concentrations near the surface of the tropical Atlantic (Cape Verde Abyssal
174 Plain) were 8.5 pg L⁻¹ (Table S12), with \sum_{ICES} PCBs (PCB-28, 52, 90/101, 118, 138, 153
175 and 180) of 6.2 pg L⁻¹; they constituted ~73% of all the \sum_{14} PCBs detected. \sum_{14} PCBs was
176 close to the high end of reported value of (\sum_{27} PCBs, 0.24-5.7 pg L⁻¹) by Gioia et al.¹¹ but
177 lower than the measurement (\sum_{36} PCBs North Atlantic, 26 pg L⁻¹) by Iwata et al.¹²
178 \sum_{ICES} PCBs was larger than (mean 2.5 pg L⁻¹) by Lohmann et al.¹³ and (0.071-1.7 pg L⁻¹)
179 by Gioia et al.¹¹

180 HCB concentration was found at 6.0 pg L⁻¹ near surface, higher than what was found in
181 the North Atlantic (0.1-3 pg L⁻¹) by Lohmann et al.¹³ but within the range of Northern
182 Hemisphere average (2-9 pg L⁻¹) by Booij et al.¹⁴ *p,p'*-DDT, *o,p'*-DDT and *p,p'*-DDE were
183 all within the range of 0.2-0.5 pg L⁻¹, which was in agreement with North Atlantic (0.1-3
184 pg L⁻¹) by Lohmann et al.¹³ and close to the lower end of Northern Hemisphere average
185 (0.3-1.4 pg L⁻¹) by Booij et al.¹⁴ and detected near 30°N Atlantic (0.5 pg L⁻¹) by Iwata et
186 al.¹²

187 The only detectable PBDEs were 47, 100 and 99. Concentrations were 1.4, 0.3 and 1.6
188 pg L^{-1} , slightly higher than ($\sim 0.5 \text{ pg L}^{-1}$ for 47 and around 0.1 pg L^{-1} for 99 and 100) by
189 Lohmann et al.¹⁵ and (0.02-1.05, nd-0.11 and $0.01\text{-}0.53 \text{ pg L}^{-1}$ respectively) by Xie et al.¹⁶

190 Detected $\Sigma_7\text{PAHs}$ was 83 pg L^{-1} near surface at the tropical Atlantic. This is within the
191 range ($\Sigma_{10}\text{PAHs}$, $58\text{-}1070 \text{ pg L}^{-1}$) reported by Nizzetto et al.¹⁷ near the northwest coast of
192 Africa, which was potentially influenced by emerging oil industry, biomass burning and
193 natural source of PAHs in Africa. PAH concentrations measured here were lower than
194 ($\Sigma_3\text{PAHs}$, average of 270 pg L^{-1}) by Lohmann et al.¹⁸ near the coast of North America. As
195 to individual PAHs, phenanthrene, fluoranthene and pyrene were dominant, which is in
196 agreement with other studies.^{17,18}

197

198 *North Atlantic*

199 In the North Atlantic (Fram Strait), surface ΣPCBs concentration of the dissolved phase
200 was 0.8 pg L^{-1} in this study (Figure 3 & Table S12), which was comparable to what was
201 observed for $\Sigma_7\text{PCBs}$ (0.7 pg L^{-1})⁴ and $\Sigma_6\text{PCBs}$ ($< 1 \text{ pg L}^{-1}$)¹⁹. As for individual congeners,
202 the highest concentration was determined by PCB-28, followed by 18, 44, 52 and then 101,
203 138, 153. This result is in agreement with result from Gioia et al.¹⁹ PCB-18, 28, 52, 101,
204 118, 138, 153 were the most detected congeners in previous studies; they were also the
205 dominant PCBs in this study.

206 HCB was the OCP detected at the highest concentration. The near surface concentration
207 was 10 pg L^{-1} , higher than those reported from the North Atlantic Bloom Experiment
208 (NABE)²⁰ but close to results from the RV Polarstern cruise ARK-XX (high Arctic, $4\text{-}10$
209 pg L^{-1}),²¹ results for the East Atlantic Ocean ($2\text{-}9 \text{ pg L}^{-1}$)¹⁴ and for the Arctic Ocean (7 pg

210 L^{-1}).²² It was mentioned by Lohmann et al.²¹ that $[\text{HCB}]_{\text{diss}}$ was negatively correlated with
211 water temperature (T_w): $[\text{HCB}]_{\text{diss}} = 6.4 - 0.57 \times T_w$. Considering the higher averaged
212 temperature from the NABE study (10 °C), $[\text{HCB}]_{\text{diss}}$ was close to the other reported values
213 after temperature corrections.

214 There were no HCHs detected, possibly due to the less hydrophobic nature of HCHs
215 which reduced their uptake by PEs. *p,p'*-DDE and *p,p'*-DDD are two breakdown products
216 of *p,p'*-DDT. Their concentrations were around 0.1-0.4 pg L^{-1} , which were also close to
217 previous studies.^{20,21} *p,p'*-DDT concentration was lower than *p,p'*-DDE and *p,p'*-DDD,
218 indicating that there is no new source of *p,p'*-DDT to the central Arctic Basin.

219 The only PBDEs detected were BDE-99 and BDE-100. Surface seawater concentrations
220 in the dissolved phase were 0.4 pg L^{-1} and 0.025 pg L^{-1} , respectively. Concentrations were
221 similar to those observed in the Asian Arctic by Möller et al.²³ While BDE-47 was one of
222 the dominant PBDEs in the other studies, it was not detected in Fram Strait (this study).

223 ΣPAHs was 148 pg L^{-1} , higher than (16-65 pg L^{-1}) by Schulz-Bull et al.²⁴ PAH
224 compounds detected tend to vary among studies conducted at different regions. Among all
225 the PAHs, fluoranthene was the one more consistently detected. Concentration of
226 fluoranthene at 213 m (94 pg L^{-1}) in this study fell in the range of other studies^{2,21} in the
227 same region.

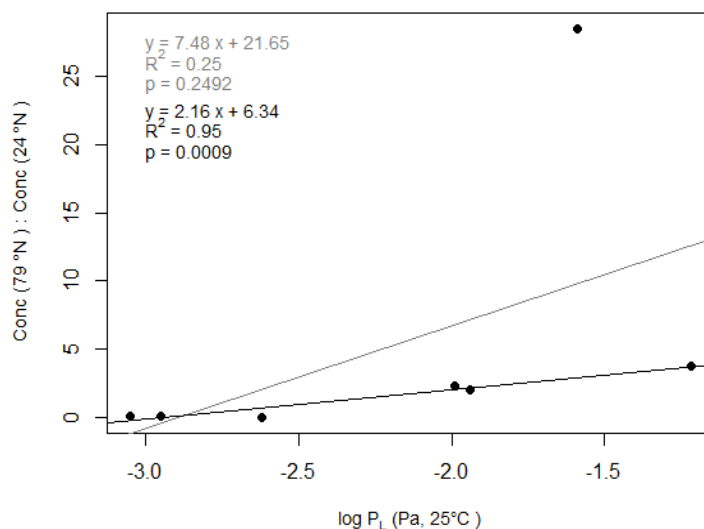
228 In summary, the concentrations of various POPs near the surface of the tropical and
229 northern Atlantic were in agreement with previous measurements reported for the remote
230 Atlantic. Comparisons (sampling year, sampling location, etc) are summarized in Table
231 S13. Overall, the comparison validates the use of PE samplers and the derived
232 concentrations.

233 A detailed discussion on the certainty of estimated concentrations can be found in the
234 Supporting Information.

235

236 **Latitudinal fractionation**

237 Next, we investigated whether there are large scale trends in PCB profiles reflecting global
238 processes. As our sampling sites are not directly linked by one major current, any
239 differences in PCB profiles should mainly stem from atmospheric deposition to the surface
240 ocean. As discussed in the methods, linear regression was used to investigate whether there
241 was a trend of the ratio of the compounds detected at the two sites and their physico-
242 chemical properties. Results are given in Figure 2. The overall correlation was not strong
243 ($R^2 = 0.25$, $p\text{-value} = 0.25$), due to an outlier (PCB-28). An outlier was defined as a value
244 outside of 1.5 times of interquartile distance ($IQD = Q3 - Q1$) subtracted from or added to
245 the first quartile ($Q1$) and the third quartile ($Q3$).²⁵ A significant higher concentration of
246 PCB-28 in the north could be resulted from an unknown emission source near the sampling
247 area. After removing PCB-28, the correlation between north-south ratio of POP
248 concentrations and $\log P_L$ was much improved ($R^2 = 0.95$) and became significant ($p\text{-value}$
249 $= 0.001$). The results imply that higher mobility compounds (higher $\log P_L$) display a
250 relatively greater abundance up north than compounds with lower mobility. This supports
251 the ideas formulated in the cold condensation theory, driven by large-scale atmospheric
252 transport.²⁶ Our results agreed with an increasing trend of concentration ratios of PCBs
253 ($88^\circ \text{ N} : 62^\circ \text{ N}$) along with \log vapor pressure observed by Sobek and Gustafsson.²⁷ We
254 note, however, that the two samples we used for the comparison were not real surface
255 samples, especially for North Atlantic site.



256
 257 **Figure 2.** Ratio of the concentration at 79° N and 24° N for PCBs detected at the depth
 258 nearest to the surface at both sites, as a function of log sub-cooled liquid vapor pressure
 259 (Pa) at 25 °C (Table S2). (Grey: all detected PCBs; Black: PCB-28 removed)

260

261 **Depth profile - comparison with the other deep ocean POP measurements**

262 Depth profiles were plotted as in Figure 3 (values are given in Table S12). Comparisons
 263 were made with the other two studies: Booij et al.² and Schulz-Bull et al.²⁴. Good agreement
 264 was achieved between the three studies. In the tropical Atlantic Ocean, most dissolved
 265 PCBs were detected at ~100 fg/L level with a few major PCBs (e.g. PCB-101,118,
 266 153,138) detected at concentrations larger than 1,000 fg/L, HCB at around 6,000 fg/L and
 267 PAHs within 1-200 fg/L . In the North Atlantic Ocean, PCBs were at ~100 fg/L, HCB at
 268 ~10,000 fg/L in the upper water column and PAHs within 1-100 pg/L (North Atlantic).
 269 Details are given in Table S14.

270

271 **Depth profile - Tropical Atlantic site**

272 *Depth profile shapes*

273 PCBs, OCPs and PAHs congeners displayed similar depth profiles; mostly with a
274 maximum at 800 m. Vertical profiles for PBDE are significantly different from the other
275 compounds. All BDEs congeners exhibited a drastic decline in truly dissolved
276 concentrations below ~250 m. Little BDEs were detected at depth, possibly linked to the
277 fact that production of BDEs peaked 20~30 years later than those for PCBs and OCPs.
278 Thus, PCBs and OCPs had more time to penetrate the deeper layers of the oceans, while
279 PBDEs have only touched the surface ocean.

280

281 *Explanations for depth profile*

282 No measurements were done above 1400 m at the Canary Basin site of Booij et al.² and
283 due to the similar concentrations found near the surface at other locations in the Atlantic,
284 the authors concluded that no large concentration gradients existed in the upper 1400 m at
285 Canary Basin. However, in the present study, a concentration maximum existed at 800 m
286 which was significantly different from the other depths. We note that neither study was
287 able to fully resolve depth profiles satisfactorily as only a few samplers were deployed,
288 potentially missing important vertical features in POPs concentration. In the present study,
289 sampling depths were restricted to specific coupling points in the mooring line, thus we
290 were not able to add more in addition to the present stations.

291 Two reasons were investigated to explain the shapes of the PCBs, OCPs and PAHs depth
292 profiles: i) Particle binding/sinking; and ii) Water current transport. Chemicals with higher
293 K_{ow} (partitioning coefficient between octanol and water) tend to bind to particles more
294 strongly. With particles sinking and getting remineralized in the deep ocean, POPs are

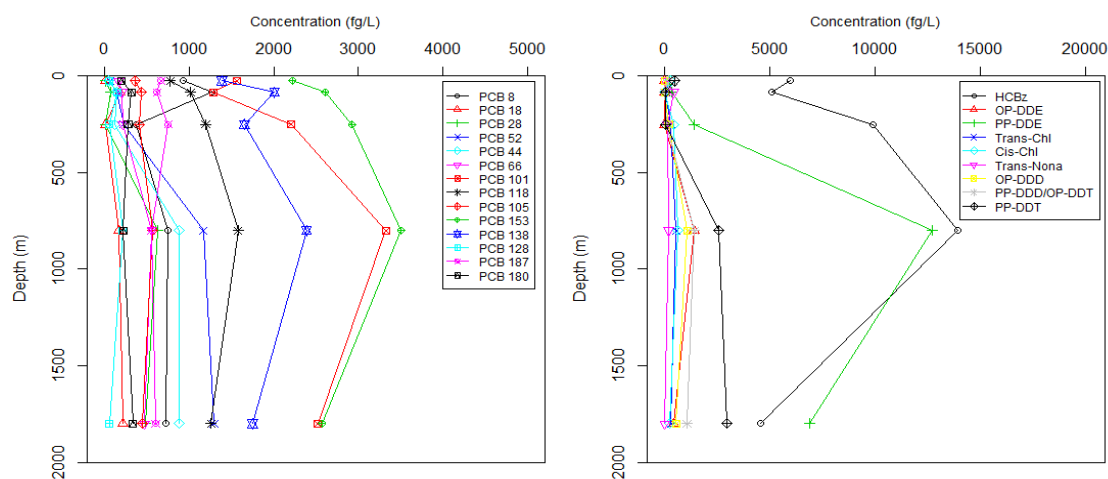
295 released back into the water. PCBs, for instances, have different levels of chlorination and
296 those with high chlorination degrees have higher tendency to bind to particles. The
297 composition from different PCBs chlorination groups were plotted in Figure S3. There is
298 an increase of di- and tri-PCBs with depth, particularly at 800 m and below. No trend of
299 increasing contribution from higher chlorinated-PCBs can be seen, suggesting that particle
300 binding/sinking processes did not dominate the 800 m maximum in PCB concentrations.
301 We note that greatest concentrations of hexa- and hepta-chlorinated congeners were found
302 in the surface samples of the tropical Atlantic, not at depth. Once exported from the surface
303 Ocean, photodegradation will not affect PCBs any longer. There is little evidence that
304 biodegradation has affected PCBs, in light of concentrations profiles with depth that are
305 not decreasing. Booij et al.² also pointed out that particle-associated transport is
306 insignificant in transferring contaminants to the deep ocean.

307 The existence of Mediterranean water has been observed in East Atlantic.²⁸
308 Mediterranean water sinks and mixes with Eastern Atlantic water after it flows out of the
309 Strait of Gibraltar, reaches equilibrium around 1000 m in depth and spreads across the
310 North Atlantic. So-called 'Meddies' are anticyclonic rings that were formed after
311 Mediterranean water flows out of the Strait of Gibraltar. They are 100 km in diameter and
312 800 m in thickness and could last as long as two or more years. It was estimated that some
313 25% of the Mediterranean outflow originates in Meddies and this makes Meddies one tool
314 to trace Mediterranean water.²⁹ Meddies are normally associated with temperature and
315 salinity anomalies, resulting from the warmer, saltier and younger feature of Mediterranean
316 water. Figure S5 is the vertical section along East Atlantic. There is anomaly at 24.58°N,
317 800 m in depth in all vertical profiles in Figure S5. Temperature, salinity and CFC-11 data

indicated a ring of warmer, saltier and younger water mass than surroundings. Although our sampling location was not exactly the same as where the anomaly occurred, considering the size of Meddies and the close proximity of these two locations, intruding from Mediterranean water cannot be ruled out.

Another evidence towards the influence of Mediterranean water on the sampler at 800 m in depth is the comparison to reported POPs in the Mediterranean water. From the study conducted in 2006-2007, concentrations in seawater were reported as $\sum_{41}\text{PCBs}$ 2-84 pg L^{-1} and HCB up to 1.7 pg L^{-1} in the Mediterranean Sea and Black Sea.³⁰ The importance of penta- and hexa-chlorinated biphenyls were in agreement with tropical Atlantic samples reported here. Reported concentration of HCB in coastal water of Alexandria, Egypt were much higher (surface water: 27 pg L^{-1}).³¹

The implication from our results is that the upper 1800 m of the water column was not well mixed with respect to POPs concentrations, and there were multiple water layers which potentially had different water mass origins, possibly affecting POPs concentrations and profiles.



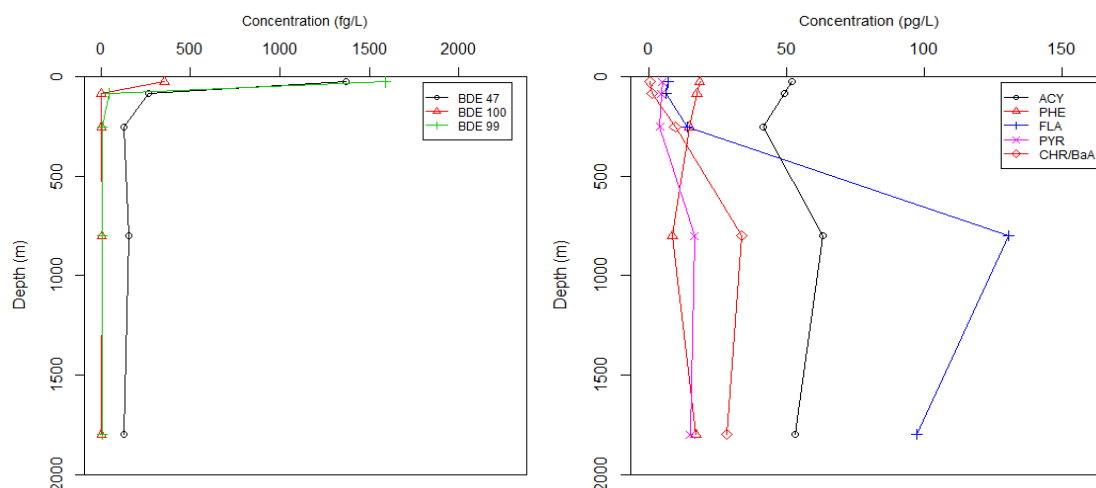


Figure 3. Depth profiles of POPs (PCBs, OCPs, PBDEs and PAHs) in the tropical

Atlantic. Lines are for connecting points only and do not represent any measurements.

Depth profile - North Atlantic site

Depth Profile Shapes

Depth profiles were plotted as in Figure 4 (values are given in Table S12). Most compounds showed similar depth profiles, such as PCBs, HCB and BDE 99. They exhibited a general decrease trend towards the deep and some maximum concentration appearing at 500 m in depth. Decreasing profiles of PCBs^{3,24} and PAHs²⁴ were observed in the 1990s in North Atlantic, while a nutrient-like profile was shown recently addressing the importance of advective flow-off from the continental shelf.⁴ The distribution pattern observed in this study neither follows a decreasing nor an increasing trend. Different distribution patterns observed for the other compounds can be partly explained by their separate degradation processes and emission pathways.

Explanations for depth profile

351 Similar to the discussion above, particle binding and sinking origination was tested by
352 PCBs chlorination composition plotted in Figure S3. Compared to the results from the
353 tropical Atlantic site, smaller degrees of chlorination tend to yield larger contribution of
354 the Σ PCBs in the North Atlantic, which means the contribution from each group has the
355 order of tri- > tetra- > penta- > hexa- . This composition pattern of chlorinated groups are
356 in line with other studies.^{4,19} No significant fraction of higher chlorinated PCBs was
357 observed along depth, indicating that particle sinking was not a major contributor to the
358 PCBs in depth in North Atlantic either.

359 The Fram Strait is the pathway for water exchange between the North Atlantic and the
360 Arctic Basin. Warm and saline Atlantic water flows into the Arctic Ocean at the eastern
361 side of Fram Strait; cold Arctic water flows out of the Arctic Mediterranean in the western
362 Fram Strait. Different branches of the Norwegian Atlantic Current (NwAC) converge and
363 form the West Spitsbergen Current (WSC). A significant part does not enter the Arctic
364 Ocean, mixes with the outflowing Arctic water and recirculates into the Nordic Seas.³² The
365 deep mooring site in this study was influenced by these recirculation water masses. From
366 1997 onwards, a deep oceanographic mooring array at 78°50'N³³ as well as three individual
367 moorings at the LTER (Long-Term Ecological Research) observatory HAUSGARTEN³⁴
368 were maintained in the Fram Strait. From the mooring data, it was noticed that deep water
369 (~ 2500 m deep) in the plateau area near the Fram Strait Sill (~ 0° E) reflects mixing
370 properties from two end members: the Greenland Sea Deep Water (GSDW) and the
371 Eurasian Basin Deep Water (EBDW); at mooring site HG-IV (central HAUSGARTEN
372 site), the water near bottom is almost purely EBDW. The mean flow at HG-IV is locally
373 topographically steered but does not achieve the cross sill advection.³⁵ Unlike the Tropical

Atlantic sampling site, it is hard to derive the water mass origins for certain depths at the North Atlantic sampling site due to the complexity and vigorousness in the water mixing processes.

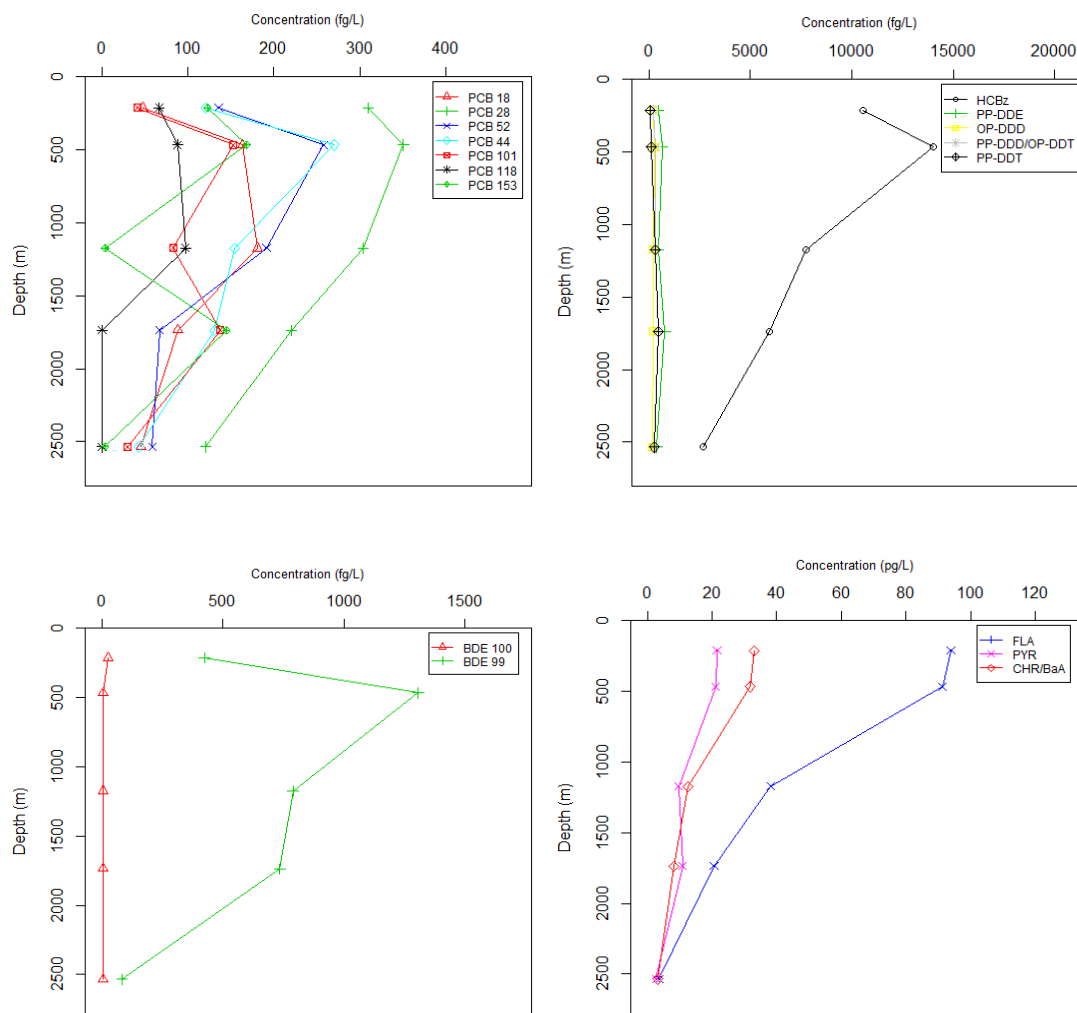


Figure 4. Depth profiles of POPs (PCBs, OCPs, PBDEs and PAHs) in the North Atlantic. Lines are for connecting points only and do not represent any measurements.

CFCs ventilation ages and plots against PCBs profiles

Tropical Atlantic

384 There was no available SF₆ data for tropical Atlantic close to our deployment period;
385 CFC-12 data were used instead to assess water mass origin and age. CFC-12 derived
386 ventilation age was plotted against the Σ PCBs in Figure S4. Detailed information for
387 ventilation age calculation was given in Table S15. The three sites chosen from CCHDO
388 for the tropical Atlantic gave close CFC-12 data throughout the water column, indicating
389 little variance of water composition around (24° N, 38° E). Ventilation age was then derived
390 by averaging out the available ventilation age from SITE1 to SITE 3 (Table S15).

391 The concentration maximum of Σ PCBs had a ventilation age of around 40 years,
392 coinciding with the peak in PCBs emission in the 1970s.³⁶ However, some other depths
393 that were not sampled may exhibit larger Σ PCBs than 800 m. It is also unknown whether
394 there is a lag in the response time of oceanic POPs to global emission, and how long it
395 might be. As discussed previously, the peak in PCB concentrations at 800 m could also be
396 due to Mediterranean water masses. Therefore, we conclude here that Σ PCBs detected at
397 the tropical Atlantic site generally followed the emission history of PCBs; yet it is unclear
398 whether the 800 m maximum reflected the 1970s PCBs emission peak.

399

400 *North Atlantic*

401 SF₆ data was used for deriving the ventilation age of water masses in the North Atlantic.
402 Large variations occurred between different sites chosen for the SF₆ data, most probably
403 resulting from the complexity in bathymetric and water current conditions in this area. The
404 closest sampling SF₆ location to our PE sampling site which also covers the whole PE
405 sampling depths was included in Table S15. Figure S4 indicated a maximum in Σ PCBs at
406 a ventilation age of ~10-20 years, younger than the maximum at tropical Atlantic site.

407 Again, due to the limited data points, it is hard to accurately determine where the Σ PCBs
408 maximum would occur. The overall distribution pattern of Σ PCBs with ventilation age still
409 followed the global emission pattern, with one peak in the middle and decrease on both
410 sides. The shift in the concentration peak of ~ 20 years could be an oceanic POPs response
411 time lag not captured by the tropical Atlantic site measurement.

412

413 **Mass balance implications for POPs in the Ocean**

414 We selected HCB for calculating mass balance in the Atlantic Ocean because the vertical
415 profiles reported here show no significant difference in absolute concentrations across the
416 Atlantic Ocean and the trend is similar. However, for PCBs, OCPs (other than HCB),
417 PBDEs and PAHs either the concentration or the trend lacks consistency between the two
418 sampling sites.

419 For HCBs, we assumed a uniform spatial distribution across the Atlantic Ocean. Pilson³⁷
420 estimated the whole surface area of Atlantic as $8.65 \times 10^7 \text{ km}^2$ with average depth of 3,700
421 m. The upper ocean (0-1,200 m) is loaded with HCB at a concentration of $9.6 \pm 3.5 \text{ pg L}^{-1}$
422 (mean \pm standard deviation), while the deep ocean (1,200-3,700 m) has a concentration of
423 $4.4 \pm 1.6 \text{ pg L}^{-1}$, based on the results of this work. The total amount of HCB residing in the
424 Atlantic Ocean is $1,947 \pm 709 \text{ t}$; it accounted for $45 \pm 16\%$ of the total HCB stored in the
425 ocean if using the estimation from Barber et al (4,300 t).³⁸ The total global production of
426 HCB was estimated as $>100,000 \text{ t}$.³⁹ The contemporary environmental burden of HCB was
427 calculated as 10,000-26,000 t.³⁸ Hence, the Atlantic Ocean stores less than 2.6 % of HCB
428 ever produced, but contains 4.8-26 % of the global HCB environmental burdens.

429

430 **IMPLICATION**

431 The current study confirmed that it is possible to deploy passive samplers to determine
432 vertical POPs gradients in the Oceans. Yet deployment times of around 1 year were
433 insufficient for most POPs to reach equilibrium in 800 and 1,600 μm thick sheets. The slow
434 equilibration was in part due to the need to use deployment cages to guarantee safe
435 deployment and retrieval of passive samplers. We were able to constrain sampling rates by
436 combining results from different thicknesses, PRC-laden sheets and modeling. Future
437 deployments would benefit from more PRC-impregnated samplers to derive in situ
438 sampling rates.

439 Results from this study supported previous work in highlighting the important role of
440 deep ocean as a compartment storing POPs. The presence of numerous POPs in deeper
441 water suggests that the deep ocean carries a significant mass already, particularly of the
442 legacy POPs. An intriguing observation from the two sites considered here is that lateral
443 water mass transport might be more important than vertical POP transport on settling
444 particles. As an example, PBDEs had penetrated the deep water masses of the Atlantic
445 Ocean to a much smaller degree than the legacy PCBs and OCPs. Clearly, additional work,
446 ideally both at numerous sites and with greater vertical resolution could help constrain the
447 importance of water mass versus particle-bound transport of POPs to depth.

448

449 **ASSOCIATED CONTENT**

450 **Supporting Information**

451 Additional details related to the physicochemical constants, sampling setup,
452 instrumental analysis, quality control and CFC information are available. This material is
453 available free of charge via the Internet at <http://pubs.acs.org>.

454

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458 **Author Contributions**

459 The manuscript was written through contributions of all authors. All authors have given
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461 **Notes**

462 The authors declare no competing financial interest.

463

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TOC Art

